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GB A 2073775

GB 1274465

GB A 2073249 GB A 2022137 GB 1269342 GB 1236698

GB A 2022137 GB 1294336

GB 1221584

(58) Field of search C7A

(54) Process for preparing a high strength stainless steel material having excellent workability and free from weld softening

(57) A stainless steel which exhibits substantially martensitic structure at room temperature is heated at a temperature of 550 to 675°C for 1 to 30 hours. A reverse-transformed austenite phase appears and a stainless steel having high strength and high elongation and being free from weld softening is obtained.

The composition of the steel lies within the range:

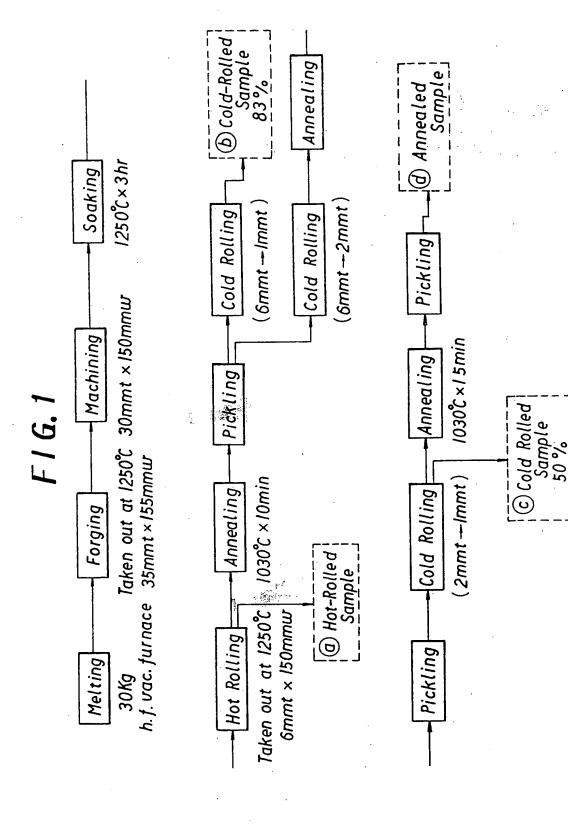
%
C 0.10 max
Si 0.20 – 4.5 V
Mn 0.20 – 5.0 V
P 0.060 max
S 0.030 max
Cr 10.0 – 17.0
Ni 3.0 – 8.0 /
N 0.10 max
Fe and impurities Bal

Up to 4% in total of Cu, Mo, W and Co may be present with up to 1% in total of Ti, Nb, V, Zr, Al and B. The relationship

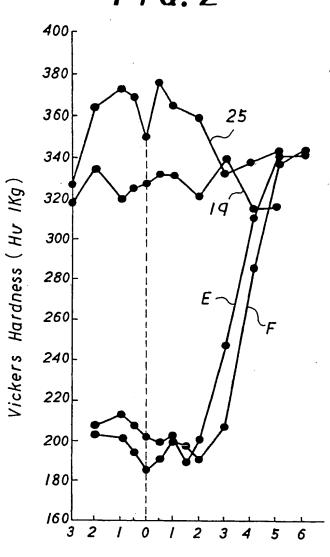
 $Ni_{eo} = 13.0 \text{ to } 17.5 = Ni + Mn + 0.5G + 0.3Si + 20[C + N]$

must also be satisfied.

UD 2 1/3 U/3 /



F1G.2



Distance from Center of Bead (mm)

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SPECIFICATION

Title of the Invention

Process for preparing a high strength stainless steel material having excellent workability and free from weld 5 softening

Field of the Invention

This invention relates to a high strength stainless steel material having excellent workability and resistance to softening by welding.

Background of the Invention

Conventional high strength stainless steels are roughly classified into (1) martensitic stainless steels, (2) work-hardenable austenitic stainless steels, and (3) precipitation-hardenable stainless steels.

Martensitic stainless steels mainly comprise Fe-Cr-C system and are substantially of single austenitic phase at 15 the quenching temperature (which is 900–1100°C, but varies depending on the content of Cr and C), but their martensite start point (Ms point) is higher than the room temperature range and they are so-called quench-hardenable steels.

These steels are hard and poor in workability in the quenched state or the quenched and tempered state. Therefore, in these steels, working such as bending, machining and cutting is carried out in the annealed state and high strength is provided by a heat-treatment such as quenching and tempering after the steel is shaped as desired. However, heat-treatment of large parts or members is difficult, and these steel materials are susceptible to weld cracking, and, therefore, tempering must be carried out after welding.

When martensitic stainless steels are to be used as structural members, the above-mentioned defects must be compensated for. To this end, a steel in which the C content is restricted lower so that a massive martensite phase appears in the quenched state has been considered. The steel of Japanese Patent Publication No. 51-35447 (1976) is an example of such a steel. A steel which falls within the claim of said patent publication is presented in No. 33 of "Nisshin Seiko Giho (Technical Reports of Nisshin Steel Co.)" (December 1975 issue). The composition thereof is: C: 0.032 %, Si: 0.75%, Mn: 0.14%, Ni: 4.01%, Cr: 12.4%, and Ti: 0.31%. This material has a tensile strength of about 108 kgf/mm² and an elongation of about 6%, and that is very low in weld softening and fight tensile strength are desirable for a welded structural material.

30 softening. Although low weld softening and high tensile strength are desirable for a welded structural material, the steel is still unsatisfactory as a structural material to be worked since elongation is poor and cracking easily occurs even in light working.
Work-hardenable austenitic stainless steels have the metastable austenitic phase as represented by AISI 301,

201, 304, 202, etc., and are hardened by cold working. Mechanical properties attained by this cold working are stipulated in JIS G 4307. For instance, in 1/2H of AISI 301, it is specified that yield strength is not less than 77 kgf/mm², tensile strength is not less than 105 kgf/mm² and elongation is not less than 10%. That is, both tensile strength and elongation are specified as being high. However, the materials of this class have a defect in that when they undergo heat input such as welding, the heated part or weld softens. Also in some cases, chromium carbide deposit in the part heated by welding, and chromium-poor layers are formed and thus intergranular stress 40 corrosion cracking occurs.

Precipitation-hardenable stainless steels are classified into martensite type, ferrite type and austenite type in accordance with the structure of the matrix. But all of them contain at least one of A1, Ti, Nb, Cu, Mo, V, etc., which contribute to age-hardening, and the steels are hardened by precipitation of intermetallic compounds caused by aging from the super-saturated solid-solution state. These steels have a tensile strength of 140 – 190 kgf/mm² and an elongation of 2 – 5%, depending upon the state of the matrix, contents of the elements which contribute to age-hardening, etc.

When these steels are used for structural members, generally working and welding are effected prior to age-hardening. However, it is difficult to age-harden larger structural members.

As has been described, the materials conventionally known as high strength stainless steels do not possess all 50 of strength, workability and resistance to weld softening.

The object of the present invention is to provide a novel high strength steel material free from the above-described defects. The object is achieved by heating a steel material of a martensitic structure, which is in a specific composition range and that satisfies a specific composition relationship, to cause reverse austenitic transformation and stabilize the thus formed reverse-transformed austenite phase.

Summary of the Invention

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This invention provides process for preparing a high strength stainless steel material having excellent workability free from weld softening consisting of a single martensitic phase or a duplex phase structure of martensit and minute austenite, said process comprising heat-treating at a temperature of 550 to 675°C for 1 to 60 30 hours a hot-rolled, cold-rolled or annealed material of a steel essentially consisting of:

C: not more than 0.10%

Si: 0.20 - 4.5% Mn: 0.20 - 5.0%

P: not more than 0.060%

65 S: not more than 0.030%

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Cr: 10.0 - 17.0% Ni: 3.0 - 8.0%

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N: not more than 0.10%

and Fe and inevitable incidental impurities, wherein the Ni_{eq} value defined as:

 $5 \text{ Ni}_{eq} = \text{Ni} + \text{Mn} + 0.5\text{Cr} + 0.3\text{Si} + 20(\text{C} + \text{N})$ is in the range of 13.0 - 17.5

This invention also provides processes for preparing similar steel materials using steels which contain in addition to the above-described components not more than 4% in total of at least one of Cu, Mo, W, and Co and/or not more than 1% in total of at least one of Ti, Nb, V, Zr, A1 and B, wherein the definition of Nies is modified in accordance with the composition.

When at least one of Cu, Mo, W and Co is contained, the Niea value is defined as:

 $Ni_{eq} = Ni + Mn + 0.5Cr + 0.3Si + 20(C + N) +$

Cu + Mo + W + 0.2Co

When at least one of Ti, Nb, V, Zr, Al and B is contained, the Nieg value is defined as :

 $Ni_{eq} = Ni + Mn + 0.5Cr + 0.3Si$

When at least one of Cu, Mo, W and Co and at least one of Ti, Nb, V, Zr, Al and B are contained, the Niea value is defined as:

 $Ni_{eq} = Ni + Mn + 0.5Cr + 0.3Si + Cu + Mo + W + 0.2Co$

The steel preferably contains 0.005 - 0.08% and more preferably 0.010 - 0.06% C; preferably 0.25 - 4.0% and more preferably 0.40 – 4.00% Si; preferably 0.30 – 4.50% and more preferably 0.40 – 4.0% Mn; preferably not 20 more than 0.040% and more preferably not more than 0.035% P; preferably not more than 0.02% and more preferably not more than 0.015% S; preferably 11.0 - 16.0% and more preferably 12.0 - 15.0% Cr; preferably 3.5-7.5% and more preferably 4 - 7.5% Ni; preferably not more than 0.07% and more preferably not more than 0.05% N; preferably 0.5 - 3.5% and more preferably 1.0 - 3.0% of at least one of Cu, Mo, W and Co when contained; and preferably 0.1 - 0.8% and more preferably 0.15 - 0.8% of at least one of Ti, Nb, V, Zr, Al and B 25 when contained.

The above-mentioned steel for the process of the present invention exhibits substantially martensitic structure in any of the hot-rolled state, cold-rolled state and annealed state, as a result of adjusting the composition so that the Ni_{eq} value as defined above is in the above-defined range.

This invention is based on the inventors' finding that the above-mentioned steel, as hot-rolled, as cold-rolled 30 or as cold-rolled and annealed, undergoes reverse austenitic transformation and stabilized by heat-treating the steel at a temperature of 550 - 675°C for 1 - 30 hours. The mechanism involved and reason for it are not yet well understood, but it has been confirmed that this reverse austenitic transformation occurs with reproducibility. Modification of the properties of stainless steel of martensitic structure by such a treatment has never been attempted before.

The steel material of the present invention exhibits a strength level of about 100 kgf/mm² and an elongation of about 20%, and does not suffer from weld softening.

The reason why the composition of the steel is defined in the claim in the present invention is as follows:

C: C is an austenite former, and effective for formation of austenite phase at high temperatures, and is also effective for strengthening the reverse transformed austenite phase and martensite phase after the heat treatment. 40 However, a larger amount of C impairs elongation, and deteriorates corrosion resistance of the weld. Therefore, it is limited to 0.10%.

N: Like C, N is an austenite former, effective for formation of the austenite phase at high temperatures, and also hardens the reverse transformed austenite phase, and is therefore, effective for strengthening the steel. However, a larger amount of N deteriorates elongation. Therefore, N is limited to 0.1%.

Si: Si is effective for strengthening the reverse transformed austenite after the heat treatment and is effective for broadening the allowable temperature range for heat treatment. For this purpose, at least 0.2% Si is required. However, a large amount of Si promotes solidification cracking when the steel is solidified or welded. Therefore, the upper limit of the Si content is defined as 4.5%.

Mn: Mn is an austenite former and necessary for adjustment of the Ms point. For this purpose, at least 0.2% 50 Mn is required. But a larger amount of Mn causes troubles in the course of steelmaking and therefore its upper limit is defined as 5%.

Cr: Cr is a fundamental component for providing the steel with corrosion resistance. However, with less than 10%, no effect can be expected, while more than 17% of Cr requires a larger amount of austenite former elements in order to produce a single austenite phase at high temperatures. The upper limit of Cr is defined as 17% so that 55 the desired structure is obtained when the steel is brought to room temperature.

Ni: Ni is an austenite former, and is necessary for obtaining a single austenite phase at high temperatures and adjustment of the Ms point. The Ni content depends on the contents of the other elements. At least about 3% of Ni is required for obtaining a single austenite phase at high temperatures and adjustment of the Ms point. Even if the contents of the other elements are reduced, more than 8% of Ni does not give the desired structure.

P: P is an inevitable impurity element incidental to principal and auxiliary raw materials. P makes steels brittle and therefore it is limited to 0.060% at the highest.

S: S is also an in vitable impurity element incidental to principal and auxiliary raw materials in steelmaking. S also mak is steels brittle and their fore it is limited to 0.030% at the highest.

Cu: Cu is inherently effective for improving corrosion resistance. In the present invention Cu is effective for 65 lowering the Ms point. Howev r, if it is contained in an amount in excess of about 4%, workability at high

temperature is impaired. Therefore, its content is limited to 4%.

Mo: Mo improves corrosion resistance and is effective for strengthening the reverse transformed austenite and lowering the Ms point. However, Mo is an expensive element and its content is limited to 4% in consideration of the cost of the steel.

W: W is effective for improving corrosion resistance and strength of the steel, and is also effective for lowering the Ms point. However, the upper limit is defined as 4%, since it raises the cost of the steel if it is contained in a larger amount.

Co: Co has a high austenitizing effect at the high temperature range, and lowers the Ms point. (Although this element has high austenitizing effect, it does not lower the Ms point excessively.) Co is very effective for 10 adjustment of composition in a high Cr content system. But the upper limit on the content thereof is defined as 4%, since it raises the cost of the steel if it is contained in a larger amount.

The last four elements mentioned above improve corrosion resistance and are effective for adjusting the martensite-forming ability of the steel in relation with the other components. They are equivalent in this sense.

Ti: Ti is a carbide-former and effective for preventing formation of Cr-poor layers caused by deposition of the carbide in welding and inhibition of grain growth of the reverse transformed austenite phase. However, if this is contained in a large amount, it may cause surface defects and may form a larger amount of scum in welding. Therefore, the Ti content is limited to 1%.

Nb: Nb is effective for preventing formation of Cr-poor layers caused by precipitation of Cr carbide in welding and inhibition of grain growth of the reverse transformed austenite phase. If it is contained in a larger amount,

20 however, it promotes solidification cracking when cast or welded, and also impairs ductility of the steel material. Therefore its content is limited to 1%.

V: V is effective for preventing formation of Cr-poor layers and inhibition of grain growth of the reverse transformed austenite. If it is contained in a larger amount, however, it impairs ductility of the steel. Therefore, its content is limited to 1%.

Zr: Zr is effective for preventing formation of Cr-poor layers caused by deposition of carbide in welding and inhibition of grain growth of the reverse transformed austenite phase. If it is contained in a larger amount, however, oxide type non-metallic inclusions are formed in casting and welding, and the surface properties and ductility of the steel are impaired. Therefore, its content is limited to 1%.

Al: Al has a remarkable effect for fixing N in the molten steel and inhibiting grain growth of the reverse 30 transformed austenite phase. If it is contained in a larger amount, it impairs flow of the molten metal in welding and thus makes the welding operation difficult. Therefore, the Al content is limited to 1%.

B: B is effective for inhibition of grain growth of the reverse transformed austenite and improvement of hot workability of the steel. If it is contained in a larger amount, however, it impairs ductility of the steel. Therefore, its content is limited to 1%.

The last six elements mentioned above are carbide formers, and remarkably effective in inhibiting grain growth of the reverse transformed austenite. In this sense, these six elements are equivalent.

The reason for defining the nickel equivalent (Ni_{eq}) as defined in the claims is as follows. In the steel used for the present invention, the temperature at which the martensite transformation is finished must be around room temperature (150 – -10°C). The steel used in the process of the present invention is of single austenite phase in the temperature range to which the steel is exposed during hot rolling, annealing or welding. But the steel must be substantially transformed into the martensite structure when the steel is brought down to room temperature from the above-mentioned condition. Here the term "substantially" means that a small amount (approximately 25%) of austenite may be retained. The amount of such remaining austenite need not be strictly considered.

In the steel used in the present invention, various elements are alloyed. We have found that insofar as the composition of the steel falls within the above-described composition range and that the nickel equivalent (Ni_{eq}) thereof as defined above is in the above-described range, the steel is of substantially martensite structure at room temperature and the object of the invention as described in the beginning of this specification is achieved.

That is to say, even though the composition is within the above-defined range, if the nickel equivalent is less than 13, the Ms point is too high and the desired high elongation cannot be obtained even if the steel is

50 heat-treated as defined above. If the nickel equivalent is greater than 17.5, the steel softens at the weld when it is welded, and thus the desired high strength members cannot be obtained. Needless to say, the formula for Ni_{eq} was defined by considering the degree of contribution of each element to the austenite-martensite transformation and thus determining each coefficient as the equivalent of the Ni amount in comparison with the degree of the contribution of Ni. Ti and the five elements that follow are neutral with respect to the

55 above-described property, and that cancel the austenite-forming ability of C and N. Therefore, in the steels

The reason f r defining the heat treatment conditions as defined in the present invention is as follows:

which contain these elements, these elements and C and N are not taken into consideration.

The steels which are of the martensite structure (massive martensite) in the annealed state have around 100 kgf/mm² of tensile strength. But as their elongation is about 6% at the utmost, it cannot be said that they have 60 satisfactory workability. When the steels are kept at a temperature in a range of 550 – 675°C for 1 – 30 hours so that part of martensite is reverse-transformed to austenite, the thus formed austenite is more or less stable as a structure, not all thereof returns to martensite in the cooling that follows, and may remain as austenite. At any rate, this heat-treatment confer high ductility to the steel without remarkably lowering strength (yield strength). At temperatures lower than 550°C, the heat treatment does not effectively bring about this ductility, and at 65 temperatures higher than 675°C, yield strength as well as ductility are impaired.

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The time of the heat treatment is suitably selected by taking the size of the material to be treated into consideration. A heat treatment over 30 hours is disadvantageous since it raises the cost of the steel.

The steel material of the present invention is suitable for manufacturing structural parts and members as well as steel belt. The steel material possesses high strength, high ductility and does not suffer weld softening.

Now the invention will be explained specifically by way of working examples with reference to the attached drawings.

Brief Explanation of the Attached Drawings

Figure 1 is a flow chart illustrating preparation of samples in the present invention, and Figure 2 is a diagram 10 showing the softening at the weld in samples of the present invention and comparative examples.

Description of Specific Embodiments of the Invention

Sample steel heats were prepared using a vacuum high frequency furnace of 30 kg capacity by the usual process, and cast into ingots 110 × 110 mm at the bottom plane, 120 × 120 mm at the top plane and 290 mm 15 in height. The ingots were forged into plates 35 mm in thickness and 155 mm in width at 1250°C, and the plates were machined into plates measuring 30 mm × 150 mm. The plates were heated at 1250°C in a soaking pit and thereafter hot-rolled to 6 mm of thickness. A portion thereof was tested as hot-rolled samples (a), and the oth r portion was annealed at 1030°C for 10 minutes, pickled and cold-rolled into sheet of 1 mm thickness (83% reduction), a portion thereof was tested as cold-rolled sample (b). The remaining portion was cold rolled to 2

20 mm thick sheets and further cold-rolled after intermediate annealing to 1 mm thick sheets (50% reduction) and a portion thereof was tested as 50% reduction cold-rolled sheet samples (c). The remaining portion was further annealed at 1030°C for 1.5 minutes and pickled. These were tested as annealed samples (d). Procedures of preparing samples are illustrated in Figure 1.

The compositions of the samples of this invention and the comparative samples are indicated in Table 1.

25 Sample Nos. 1 – 32 are steels used in the process of this invention and Nos. A – F are steels of comparative examples. The compositions of these samples are within the defined composition range, but the nickel equivalent Ni_{eq} of Samples A – D are less than 13 and those of Samples E – F is greater than 17.5.

Mechanical property tests were carried out using test pieces No. 5 and No. 13B stipulated in JIS Z 2201. The amount of martensite was measured using a vibrating sample magnetometer.

30 Mechanical properties and the amount of martensite of the samples are summarized in Table 2. In Table 2, "Conventional Process" means that the heat treatment in accordance with this invention was not carried out. According to Table 2, the steels which were not heat-treated in accordance with the present invention and exhibit a substantially massive martensite structure in the annealed state have high level strength such as yield strengths of 73 – 126 kgf/mm² and tensile strengths of 94 – 135 kgf/mm², but their elongation is at the utmost

35 7.0%. This is remarkably low in comparison with Sample E and F, which are 20% cold-rolled sheets. Even among the samples which underwent the heat treatment of the present invention, those of the comparative steels have only 8.5% elongation at the highest, though even this is some improvement. The samples of the present invention exhibit generally remarkable improvement in elongation while retaining yield strength, although some samples suffer slight decrease in yield strength.

The mechanical properties and the amounts of martensite when annealed samples (d) were heat-treated under various conditions are shown in Table 3. "Comparative Process" in Table 3 means examples in which samples were heat-treated at temperatures in excess of the heat treatment temperature range of the present invention. From Table 3, it is learned that there is a criticality around the upper limit heat treatment temperature of 675°C.

The welding test was carried out by laying a bead on 1 mm thick plates by TIG welding with 50 A electric 45 current at a rate of 400 mm/min. The results are shown in Figure 2. Figure 2 shows hardness distribution profile from the center of beads. Sample 19 and 25, which are samples of the present invention, were heat-treated at 600°C for 20 hours. Comparative Sample E and F are 20% cold-rolled sheets. As seen in this figure, the samples of the present invention obviously do not exhibit softening at the weld.

TABLE 1

Chemical Composition and Ni_{eq} of the Steels for the Invention Process and Comparative Steels

Sample C S i		,					,	Com	Composition (wt%)	(%)	0	, i	₹	
1 0.066 0.25 158 0.027 0.009 1295 352 0.007 2 0.010 0.22 0.27 0.37 0.034 0.014 1303 6.25 0.015 5 0.021 0.22 0.30 0.027 0.007 12.7 743 0.019 6 0.011 0.24 0.37 0.034 0.014 1303 6.25 0.015 6 0.011 0.24 0.37 0.034 0.014 1303 6.25 0.010 0.016 Car 2.12 7 0.007 0.28 0.27 0.019 0.012 15.09 6.39 0.010 Car 2.12 10 0.013 0.22 0.30 0.024 0.005 12.97 747 0.011 Wr 1.84 11 0.014 0.28 0.38 0.020 0.004 13.87 747 0.011 Wr 1.84 12 0.030 0.25 0.38 0.020 0.004 13.87 743 0.015 0.015 Th 0.016 14 0.011 0.024 0.025 0.030 0.004 13.87 743 0.015 Th 0.016 15 0.024 0.25 0.38 0.020 0.001 12.99 4.98 0.015 Th 0.016 16 0.024 2.15 0.31 0.022 0.009 12.99 4.98 0.015 Th 0.016 17 0.014 0.28 0.38 0.020 0.001 13.04 7.31 0.014 Th 0.014 Th 0.026 18 0.026 0.027 0.030 0.012 13.04 7.31 0.014 Th 0.026 0.001 19 0.015 0.24 0.028 0.036 0.001 13.04 7.31 0.014 Th 0.026 0.001 19 0.016 0.32 0.040 0.037 0.008 12.92 6.67 0.002 20 0.010 0.35 0.040 0.037 0.006 13.87 7.00 0.015 Th 0.014 Th 0.049 21 0.010 0.35 0.04 0.037 0.006 13.87 7.00 0.015 Th 0.049 Th 0.037 0.006 13.87 7.00 0.015 Th 0.010 Th 0.037 0.006 13.87 7.00 0.010		Sample No.	ပ	iS	Mn	d	S	ర	, iN	<u> </u>) Cu. Ma. Co. W	71, NO. Zr. B. 1	į _	Ņ,
2 0.010 0.27 1.14 0.031 0.075 0.071 0.075 0.001 0.075 0.001 0.075 0.001 0.075 0.001 0.075 0.001 0.075 0.001 0.075 0.001 0.075 0.001 0.075 0.001 0.075 0.001 0.001 0.001 0.001 0.001 0.001		-	0.060	0.25	1.58	0.027	0.00	12.96	3.52	0.012				13.1
3 0.013 0.02 0.029 0.007 1.27 7.43 0.019 5 0.024 0.024 0.029 0.020 1.021 0.010 CC: 3.01 6 0.071 0.54 0.47 0.029 0.027 1.29 6.07 0.01 0.01 0.02 7 0.07 0.22 0.03 0.020 0.027 1.29 6.09 0.01 0.01 0.01 0.02 9 0.016 0.02 0.02 0.02 0.02 1.27 0.04 0.01 0.01 0.02 0.02 11 0.014 0.02 0.02 0.02 0.02 0.02 0.03 0.03 0.04 0.03 0.01 0.04 0.01 0.04 0.01		7	0.010	0.27	1.14	0.031	0.010	13.04	4.00	0.076				13.5
4 0.045 2.07 0.37 0.034 0.014 13.03 6.25 0.012 5 0.021 0.54 0.47 0.021 10.09 16.99 6.03 0.010 Cc. 2.12 7 0.007 0.24 0.31 0.024 0.026 1.27 0.011 10.02 0.013 0.024 0.015 1.27 0.011 Wr. 184 9 0.016 0.013 0.024 0.026 1.28 7.12 0.014 0.028 3.08 0.005 1.28 7.12 0.014 Wr. 1.08 10 0.014 0.25 2.87 0.025 0.005 1.28 0.015 0.015 Mr. 1.08 11 0.014 0.25 0.037 0.030 0.039 1.039 0.015 0.015 0.015 0.015 0.015 0.015 0.015 0.015 0.015 0.015 0.015 0.015 0.015 0.015 0.015 0.015 0.015 0.015 0.015 0.0	=	ო	0.013	0.22	0.36	0.029	0.007	12.77	7.43	0.019		4		14.9
5 0.021 0.64 0.047 0.021 0.024 0.047 0.021 0.009 0.023 0.010 0.012 0.013 0.009 0.009 0.007 1.29 0.010 0.012 0.003 0.007 1.29 0.010 0.012 0.003 0.004 0.003 0.004 1.23 0.004 0.003 0.004 1.28 3.03 0.013 0.004 0.003 0.004 1.28 3.03 0.014 0.004 0.003 0.004 1.28 3.03 0.014 0.004 0.004 0.004 1.28 3.03 0.014 0.004 0.004 0.004 1.28 3.03 0.014 0.004		4	0.045	2.07	0.37	0.034	0.014	13.03	6.25	0.012				14.9
6 0.01 0.24 0.31 0.039 0.012 1.50 6.03 0.010 Cur. 212 7 0.0007 0.28 0.27 0.007 0.004 0.006 1.29 7.47 0.011 Wr. 1.84 9 0.016 0.024 0.034 0.006 1.28 3.02 0.019 Mr. 1.84 10 0.013 0.028 0.034 0.006 1.28 3.02 0.019 Tr. 0.16 11 0.014 0.028 0.036 0.031 1.29 3.02 0.019 Tr. 0.16 Tr. 0.16 12 0.034 0.026 0.009 1.299 4.98 0.015 Tr. 0.16		ıc	0.021	0.54	0.47	0.021	0.00	16.99	5.01	0.015	Co: 3.01			15.2
7 0.007 0.28 0.27 0.019 0.007 12.91 7.40 0.001 W: 184 8 0.006 0.22 0.005 12.37 6.69 0.013 Moz.260 1.027 1.01 10 0.013 0.26 3.89 0.005 12.87 3.03 0.019 Mr. 1.08 Tr. 0.02 11 0.014 0.26 3.89 0.020 0.006 12.89 3.03 0.018 Tr. 0.16 Tr. 0.16 13 0.014 0.92 0.38 0.020 0.007 13.04 7.38 0.018 Tr. 0.16 Tr. 0.16 14 0.014 0.92 0.39 0.027 0.004 1.29 3.03 0.018 Tr. 0.16 Tr. 0.028 Tr. 0.16 1.28 0.016 Tr. 0.028 Tr. 0.16 1.00 1.00 Tr. 0.16 Tr. 0.16 Tr. 0.16 Tr. 0.16 1.00 1.00 Tr. 0.16 Tr. 0.16 Tr. 0.16 Tr. 0.16 Tr. 0.014 Tr. 0.013 Tr. 0.013		9	0.011	0.24	0.31	0.029	0.012	15.09	6.03	0.010	Cu: 2.12			16.5
8 0,006 0,22 0,30 0,024 0,005 1,27 6,69 0,013 MG, 260 1 1 1 1 0,014 0,28 380 0,027 0,004 1,382 7,12 0,014 CL, 0,76 W; 1,08 1 1 0,014 0,28 4,69 0,035 0,013 1,29 4,98 0,015 TF; 0,019 TF; 0,028 1,39 0,025 0,003 1,28 1 30 0,019 TF; 0,019 TF; 0,019 TF; 0,014 0,014 0,028 4,69 0,035 0,013 1,29 4,98 0,015 TF; 0,019 TF; 0,019 1,10 0,014 0,02 0,28 0,026 0,007 1,304 7,31 0,014 TF; 0,014 0,011 2,02 0,37 0,008 1,28 6,5 0,020 0,015 TF; 0,028 1,16 0,034 0,037 0,008 1,28 6,5 0,020 0,020 0,024 1,16 0,014 0,37 0,29 0,008 1,28 0,009 0,027 0,008 1,28 0,009 0,027 0,009 1,28 0,009 0,000 0,00	•	7	0.007	0.28	0.27	0.019	0.007	12.91	7.47	0.011	W: 1.84			16.5
9 0.019 0.41 0.33 0.027 0.004 1382 712 0.014 Cu. 0.76, W: 1.08 110 0.013 0.26 3.89 0.020 0.006 12.89 3.03 0.019 111 0.014 0.28 4.89 0.020 0.006 12.89 4.98 0.015 112 0.030 0.25 2.87 0.022 0.009 12.99 4.98 0.015 113 0.014 0.32 0.38 0.026 0.007 13.04 7.38 0.015 114 0.011 2.02 0.38 0.026 0.007 13.04 7.38 0.015 115 0.034 2.16 0.33 0.027 0.008 12.82 6.94 0.013 116 0.024 0.85 0.30 0.031 0.010 15.62 6.94 0.013 117 0.014 0.37 0.29 0.036 0.014 13.27 7.02 0.016 118 0.020 0.64 0.39 0.026 0.014 13.27 7.00 0.015 119 0.015 0.32 0.46 0.025 0.004 13.87 7.00 0.016 119 0.017 0.30 0.30 0.035 0.004 13.87 7.00 0.016 120 0.010 0.30 0.30 0.037 0.006 13.84 7.03 0.014 130 0.014 0.30 0.35 0.026 0.011 13.37 7.04 0.010 131 0.038 0.039 0.039 0.006 13.84 7.03 0.014 132 0.039 0.39 0.039 0.008 13.61 6.91 0.010 132 0.030 0.31 0.020 0.031 0.008 13.61 6.91 0.010 133 0.030 0.31 0.020 0.031 0.008 13.61 6.91 0.010 134 0.039 0.030 0.030 0.031 0.008 13.61 6.91 0.010 135 0.030 0.030 0.030 0.031 0.031 0.031 0.010 138 0.031 0.032 0.031 0.032 0.031 13.87 7.02 0.009 130 0.001 2.66 0.032 0.003 13.06 6.33 0.010 0.01 0.01 0.010 139 0.010 0.30 0.030 0.031 0.031 0.031 0.009 130 0.001 0.30 0.032 0.001 13.87 7.00 0.010 0.		œ	900'0	0.22	0.30	0.024	0.005	12.37	69.9	0.013				16.2
10 0.013 0.26 380 0.020 0.006 12.87 3.03 0.019 Tri 0.27 11 0.014 0.28 469 0.035 0.013 12.99 3.02 0.018 Tri 0.027 11 0.014 0.28 469 0.035 0.003 12.99 3.02 0.018 Tri 0.08 13 0.014 0.29 0.38 0.026 0.007 13.04 7.38 0.015 Tri 0.08 14 0.001 2.02 0.33 0.020 0.001 13.04 7.3 0.014 Tri 0.28 15 0.024 0.21 0.37 0.030 0.012 13.04 7.3 0.014 Tri 0.28 17 0.014 0.37 0.29 0.036 0.014 14.21 7.02 0.015 Tri 0.050 18 0.020 0.54 0.39 0.029 0.006 14.08 660 0.027 Ali 0.77 19 0.016 0.35 0.04 0.037 0.006 14.08 660 0.027 Ali 0.77 20 0.010 0.35 0.04 0.037 0.006 13.04 0.015 21 0.001 0.35 0.02 0.004 13.07 7.00 0.016 Tri 0.50 Ali 0.77 22 0.001 0.35 0.02 0.004 13.07 7.00 0.016 Tri 0.29 24 0.056 1.90 0.39 0.02 0.001 13.7 689 0.010 Tri 0.50 Ali 0.03 25 0.030 0.31 0.02 0.001 13.7 0.000 13.6 0.01 Tri 0.049 26 0.038 0.039 0.021 0.005 13.06 6.25 0.013 Tri 0.049 27 0.007 2.04 0.03 0.001 13.0 0.001 13.0 0.010 Tri 0.049 28 0.007 2.04 0.03 0.001 13.16 6.3 0.010 Cri 1.01 Tri 0.34 29 0.013 0.02 0.001 13.16 0.001 13.16 0.001 Tri 0.03 20 0.010 0.35 0.001 13.0 0.001 13.16 0.001 Ali 0.011 Tri 0.049 20 0.013 0.02 0.001 13.0 0.001 13.16 0.001 Ali 0.011 Tri 0.049 21 0.004 0.39 0.27 0.008 0.008 13.0 0.004 Cri 0.01 Ali 0.009 Cri 0.03 20 0.010 0.26 0.20 0.000 13.0 0.001 13.16 0.001 Ali 0.011 Tri 0.004 20 0.010 0.20 0.000 0.001 13.0 0.001 13.0 0.001 Ali 0.001		6	0.019	0.41	0.33	0.027	0.004	13.82	7.12	0.014	⋛			17.0
11 0.014 0.28 4.68 0.035 0.013 12.90 3.02 0.018 Tic 0.16 12 0.030 0.22 2.030 0.022 0.007 12.94 3.89 0.015 Tic 0.016 13 0.014 0.92 0.38 0.026 0.007 13.04 7.38 0.015 Tic 0.016 14 0.011 2.02 0.37 0.030 0.012 13.04 7.31 0.013 Tic 0.016 15 0.024 2.15 0.33 0.020 0.027 0.003 17.0 0.013 Nb. 0.01 16 0.026 0.86 0.030 0.014 14.21 7.02 0.013 Nb. 0.01 18 0.020 0.034 0.035 0.006 14.08 6.00 0.027 Nb. 0.07 20 0.011 0.025 0.014 14.21 7.00 0.016 Nb. 0.07 Nb. 0.07 21 0.011 0.025 0.026 0.014		0	0.013	0.26	3.80	0.020	900.0	12.87	3.03	0.019		-	27	13.3
12 0.030 0.25 287 0.002 0.299 4.38 0.015 Tit 0.08 14 0.014 0.92 0.32 0.020 0.020 0.017 13.04 7.31 0.015 Tit 0.08 14 0.014 0.026 0.007 13.04 7.31 0.014 Tit 0.014 Tit 0.028 16 0.026 0.85 0.30 0.031 0.010 15.22 6.67 0.029 Nb: 0.41 17 0.014 0.22 0.030 0.031 0.010 15.62 6.64 0.013 Nb: 0.42 18 0.026 0.85 0.30 0.031 0.016 15.62 6.67 0.015 Nb: 0.50 19 0.016 0.32 0.40 0.026 0.004 13.87 7.00 0.016 Nb: 0.50 20 0.016 0.32 0.040 0.037 0.041 13.87 7.00 0.016 Nb: 0.001 21 0.011 0.32 0.04		=	0.014	0.28	4.69	0.035	0.013	12.90	3.02	0.018			16	14.2
13 0.014 0.92 0.38 0.026 0.007 13.04 7.38 0.015 Ti: 0.15 14 0.014 2.02 0.37 0.030 0.012 13.04 7.31 0.014 Ti: 0.28 15 0.024 2.15 0.31 0.027 0.008 12.92 6.94 0.013 No.04 No.04 No.04 No.04 No.04 No.05 No.05 No.06 1.29 6.00 No.05 No.06 No.06 No.06 No.06 No.06 No.07 No.06 No.06 No.06 No.07 No.07 No.07 No.07 No.07 No.07 No.07 No.08 No.07 No.07 No.07 No.07 No.07 No.07 <t< td=""><td></td><td>12</td><td>0.030</td><td>0.25</td><td>2.87</td><td>0.022</td><td>0.00</td><td>12.99</td><td>4.98</td><td>0.015</td><td></td><td></td><td>80</td><td>14.4</td></t<>		12	0.030	0.25	2.87	0.022	0.00	12.99	4.98	0.015			80	14.4
14 0.011 2.02 0.37 0.030 0.012 13.04 7.31 0.014 TI: 0.28 15 0.024 2.15 0.37 0.020 0.020 0.020 ND: 0.41 16 0.0264 2.15 0.33 0.027 0.036 0.014 14.21 7.02 0.015 ND: 0.50 17 0.014 0.37 0.29 0.026 0.04 14.22 7.02 0.015 ND: 0.24 18 0.020 0.54 0.39 0.026 14.08 6.60 0.027 AI: 0.77 19 0.015 0.32 0.046 13.87 7.00 0.016 ND: 0.27 20 0.010 0.32 0.026 13.61 6.31 0.010 YO AI: 0.77 21 0.011 0.30 0.026 13.61 6.31 0.010 ND: 0.42 22 0.030 0.041 13.75 7.04 0.010 TI: 0.50 23 0.025		13	0.014	0.92	0.38	0.026	0.007	13.04	7.38	0.015		i≓ O	15	14.6
15 0.034 2.15 0.31 0.027 0.008 12.92 667 0.020 Nb: 0.41 16 0.026 0.085 0.30 0.031 0.001 15.62 6.94 0.033 Nb: 0.50 16 0.026 0.085 0.30 0.031 0.014 14.21 7.02 0.015 Nb: 0.50 18 0.020 0.029 0.029 0.026 0.004 13.87 7.00 0.016 Rb: 0.39 20 0.016 0.32 0.026 0.004 13.87 7.00 0.016 Rb: 0.39 20 0.010 0.35 0.026 0.004 13.87 7.00 0.014 Nb: 0.42 20 0.010 0.027 0.028 0.006 13.61 6.010 Nb: 0.42 Nb: 0.42 21 0.011 0.30 0.028 0.006 13.61 13.00 0.010 Nb: 0.42 Nb: 0.42 22 0.028 0.029 0.006 13.00		14	0.01	2.03	0.37	0.030	0.012	13.04	7.31	0.014		Ë	28	14.8
16 0.026 0.85 0.30 0.031 0.010 1.65 6.94 0.013 N. D.50 17 0.014 0.37 0.236 0.074 14.21 7.02 0.015 Ti: 0.67 18 0.020 0.54 0.35 0.036 0.074 14.21 7.02 0.015 Ti: 0.67 19 0.016 0.34 0.026 0.004 13.87 7.00 0.016 R: 0.07 20 0.010 0.35 0.026 0.041 13.87 7.00 0.016 V: 0.47 21 0.011 0.35 0.026 0.011 13.72 6.89 0.010 Ti: 0.07 22 0.020 0.44 0.028 0.006 13.51 0.010 Ti: 0.50 N. D.47 24 0.026 1.30 0.32 0.011 13.77 7.04 0.010 Ti: 0.50 N. D.42 25 0.026 1.30 0.026 14.61 7.36 0.010 Ti: 0.00		15	0.034	2.15	0.31	0.027	0.008	12.92	6.67	0.020		Ò N P O	41	14.1
17 0.014 0.37 0.29 0.036 0.014 14.21 7.02 0.015 TI: 0.67 18 0.020 0.54 0.39 0.029 0.006 14.08 6.60 0.027 AI: 0.77 19 0.016 0.32 0.46 0.025 0.004 13.87 7.03 0.016 B: 0.39 20 0.010 0.35 0.40 0.037 0.011 13.72 6.89 0.010 V: 0.47 21 0.011 0.30 0.34 0.026 0.011 13.72 6.89 0.010 V: 0.47 22 0.030 0.41 0.024 0.008 13.61 6.91 0.010 TI: 0.50, Nb: 0.42 23 0.026 0.42 0.028 0.006 14.61 5.36 0.010 TI: 0.10, V: 0.25 24 0.036 0.01 14.61 5.36 0.010 Cu: 1.01 TI: 0.10, V: 0.25 25 0.040 0.021 0.024 0.006 14.6		16	0.026	0.85	0.30	0.031	0.010	15.62	6.94	0.013		NP: O	20	15.3
18 0.020 0.54 0.39 0.029 0.020 0.54 0.39 0.029 0.006 14.08 6.60 0.027 Ali 0.77 19 0.015 0.32 0.46 0.025 0.004 13.87 7.00 0.016 88 0.39 20 0.010 0.35 0.46 0.025 0.006 13.64 7.03 0.014 V: 0.47 V: 0.47 21 0.011 0.30 0.35 0.028 0.006 13.61 6.91 0.010 Tri 0.50 Nb: 0.42 22 0.030 0.41 0.40 0.034 0.006 13.61 6.010 Tri 0.50 Nb: 0.42 24 0.056 1.90 0.032 0.006 14.61 7.36 0.010 Tri 0.50 Nb: 0.42 25 0.040 1.44 0.29 0.011 13.87 7.02 0.013 Tri: 0.50 Nb: 0.42 26 0.038 1.027 0.011 13.87 7.02 <td< td=""><td></td><td>17</td><td>0.014</td><td>0.37</td><td>0.29</td><td>0.036</td><td>0.014</td><td>14.21</td><td>7.02</td><td>0.015</td><td></td><td></td><td>67</td><td>14.5</td></td<>		17	0.014	0.37	0.29	0.036	0.014	14.21	7.02	0.015			67	14.5
19 0.015 0.32 0.46 0.025 0.004 13.87 7.00 0.016 B: 0.39 20 0.010 0.35 0.40 0.037 0.006 13.64 7.03 0.014 V: 0.47 21 0.011 0.35 0.40 0.037 0.006 13.64 7.03 0.010 Ti: 0.50 N: 0.42 22 0.028 0.35 0.026 0.006 13.57 7.04 0.010 Ti: 0.50 N: 0.42 24 0.028 0.39 0.021 0.006 13.57 7.04 0.010 Ti: 0.10 V: 0.47 25 0.028 0.028 0.006 14.61 7.36 0.013 Ti: 0.10 V: 0.25 26 0.038 1.52 0.011 13.87 7.02 0.008 Cu: 0.101 Ti: 0.49 27 0.007 1.04 0.028 13.16 6.33 0.011 Ti: 0.49 Ti: 0.49 Ti: 0.10 28 0.007 2.04		18	0.00	0.54	0.39	0.029	9000	14.08	9.60	0.027	•		7.	14.2
20 0.010 0.35 0.40 0.037 0.006 13.64 7.03 0.014 V: 0.47 21 0.011 0.30 0.35 0.026 0.011 13.72 6.89 0.010 Ti: 0.59 22 0.030 0.34 0.026 0.011 13.72 6.89 0.010 Ti: 0.50 Nb: 0.42 23 0.026 0.034 0.006 13.67 7.04 0.010 Ti: 0.32 AI: 0.50 24 0.056 1.90 0.03 0.021 0.006 13.67 7.04 0.010 Ti: 0.52 AI: 0.50 25 0.036 1.02 0.006 13.67 7.02 0.013 Ti: 0.10 V: 0.52 26 0.038 1.52 0.011 13.87 7.02 0.015 Mo: 1.10 Ti: 0.10 V: 0.25 27 0.007 2.04 0.024 0.008 13.16 6.33 0.015 Mo: 1.17 Ti: 0.10 Vii 0.10 28 0.007 <td></td> <td>19</td> <td>0.015</td> <td>0.32</td> <td>0.46</td> <td>0.025</td> <td>0.004</td> <td>13.87</td> <td>7.00</td> <td>0.016</td> <td></td> <td>89</td> <td>39</td> <td>14.5</td>		19	0.015	0.32	0.46	0.025	0.004	13.87	7.00	0.016		89	39	14.5
21 0.011 0.30 0.35 0.026 0.011 13.72 6.89 0.010 Zi: 0.59 22 0.030 0.41 0.40 0.034 0.008 13.61 6.91 0.010 Tri: 0.50 NB: 0.42 23 0.028 0.028 0.006 13.57 7.04 0.010 Tri: 0.32 AI: 0.56 24 0.028 0.029 0.006 13.06 6.25 0.013 Tri: 0.10, V: 0.25 25 0.040 1.44 0.29 0.018 0.006 14.61 7.36 0.010 Cu: 1.01 Tri: 0.10, V: 0.25 26 0.038 1.52 0.21 0.006 14.61 7.36 0.010 Cu: 1.01 Tri: 0.49 27 0.007 3.05 0.31 0.024 0.008 13.16 6.33 0.016 Mo: 1.77 Tri: 0.37 28 0.007 2.04 0.028 0.008 13.09 7.00 0.011 Cu: 2.03 NB: 0.45 29		20	0.010	0.35	0.40	0.037	900.0	13.64	7.03	0.014			47	14.4
22 0.030 0.41 0.40 0.034 0.008 13.61 6.91 0.010 Ti: 0.50, Nb: 0.42 23 0.028 0.035 0.42 0.028 0.006 13.57 7.04 0.010 Ti: 0.10, V: 0.25 24 0.056 1.90 0.39 0.021 0.005 14.61 7.36 0.010 Cu: 1.01 Ti: 0.10, V: 0.25 25 0.040 1.52 0.21 0.027 0.011 13.87 7.02 0.008 Cu: 1.01 Ti: 0.10, V: 0.25 26 0.037 0.011 13.87 7.02 0.008 Cu: 1.01 Ti: 0.10, V: 0.25 29 0.013 0.31 0.024 0.008 13.09 7.00 0.011 W: 0.82 Ti: 0.10, V: 0.25 29 0.013 0.37 0.28 0.008 13.09 7.00 0.010 W: 0.82 Ti: 0.10, V: 0.28 30 0.013 0.32 0.028 0.006 12.18 5.40 0.011 Cu: 1.01 Ti: 0.10		7	0.011	0.30	0.35	0.026	0.011	13.72	6.83	0.010				4.
23 0.028 0.35 0.42 0.028 0.026 13.57 7.04 0.010 Ti: 0.32, Ai: 0.50 24 0.056 1.30 0.39 0.021 0.005 13.06 6.25 0.013 Ti: 0.10, V: 0.25 25 0.040 1.44 0.29 0.018 0.006 14.61 7.36 0.010 Cu: 1.01 Ti: 0.10, V: 0.25 26 0.038 1.51 0.027 0.001 13.09 0.008 13.18 5.00 0.009 Cu: 1.01 Ti: 0.10, V: 0.25 11.049 29 0.013 0.31 0.028 0.008 13.09 7.00 0.010 W: 0.82 Ti: 0.10, Nb: 0.41 29 0.013 0.37 0.28 0.008 13.09 7.00 0.010 W: 0.82 Ti: 0.10, Nb: 0.41 30 0.010 2.56 0.24 0.028 0.006 12.82 6.12 0.014 W: 0.82 Ti: 0.58 31 0.040 1.39 0.028 0.009 12.		77	0.030	0.41	0.40	0.034	0.008	13.61	6.91	0.010				14.2
24 0.056 1.90 0.39 0.021 0.005 13.06 6.25 0.013 Ti: 0.10, V: 0.25 Ti: 0.10, V: 0.25 25 0.040 1.44 0.29 0.018 0.006 14.61 7.36 0.010 Cu: 1.01 Ti: 0.19 V: 0.25 26 0.038 1.52 0.21 0.027 0.011 13.87 7.02 0.008 Cu: 0.68, Mo: 1.02 Tr: 0.37 27 0.007 3.05 0.31 0.024 0.008 13.16 6.33 0.015 Mo: 1.77 Tr: 0.10, Nb: 0.45 29 0.013 0.37 0.26 0.028 0.008 13.09 7.00 0.011 Cu: 2.03 Nb: 0.45 30 0.010 2.56 0.24 0.028 0.006 14.56 6.37 0.009 Cc: 2.31 Ar: 0.70 31 0.040 1.39 0.023 0.008 12.82 6.12 0.014 Cc: 2.31 Ar: 0.70 32 0.026 4.12 0.099 12.28 </td <td></td> <td>23</td> <td>0.028</td> <td>0.35</td> <td>0.42</td> <td>0.028</td> <td>9000</td> <td>13.57</td> <td>7.04</td> <td>0.010</td> <td></td> <td>Ë</td> <td></td> <td>14.4</td>		23	0.028	0.35	0.42	0.028	9000	13.57	7.04	0.010		Ë		14.4
25 0.040 1.44 0.29 0.018 0.006 14.61 7.36 0.010 Cur. 1.01 Ti: 0.49 26 0.038 1.52 0.21 0.027 0.011 13.87 7.02 0.008 Cu: 0.68 Mor. 1.77 Ti: 0.10 Nb: 0.47 27 0.007 3.05 0.31 0.024 0.008 13.16 6.33 0.015 Mor. 1.77 Ti: 0.10 Nb: 0.45 29 0.007 2.04 0.028 0.008 13.09 7.00 0.010 Cu: 2.03 Nb: 0.45 31 0.040 1.39 0.24 0.028 0.006 12.82 6.12 0.014 Cu: 0.91 W: 0.82 Tr: 0.58 30 0.040 1.39 0.028 0.006 12.82 6.12 0.014 Cu: 0.91 W: 0.82 Tr: 0.58 31 0.040 1.39 0.023 0.009 12.82 6.12 0.014 Cu: 0.91 W: 0.82 Tr: 0.58 4 0.026		54	0.056	1.90	0.39	0.021	0.005	13.06	6.25	0.013		Ë		13.8
26 0.038 1.52 0.21 0.027 0.011 13.87 7.02 0.008 Cu. 0.68, Mor. 1.02 TF: 0.37 27 0.007 3.05 0.31 0.024 0.008 13.16 6.33 0.015 Mor. 1.77 TI: 0.10, NB: 0.41 28 0.007 2.04 0.30 0.032 0.012 12.18 5.40 0.011 Cu.; 2.03 NB: 0.45 39 0.010 2.56 0.24 0.028 0.006 14.56 6.37 0.009 Co; 2.31 AI: 0.58 31 0.040 1.39 0.27 0.037 0.009 12.82 6.12 0.014 Cu. 0.91, Wr. 1.97 TF: 0.81 32 0.026 4.12 0.039 12.82 6.12 0.014 Cu. 0.91, Wr. 1.97 TF: 0.81 A 0.026 4.12 0.039 13.12 7.12 0.014 Cu. 0.91, Wr. 1.97 TF: 0.81 B 0.046 0.31 0.21 0.004 11.72		22	0.040	1.44	0.29	0.018	9000	14.61	7.36	0.010		0 ≓	•	16.4
27 0.007 3.05 0.31 0.024 0.008 13.16 6.33 0.015 Mor.1.77 Ti: 0.10, Nb: 0.41 28 0.007 2.04 0.30 0.032 0.012 12.18 5.40 0.011 Cu: 2.03 Nb: 0.45 29 0.013 0.37 0.26 0.028 0.008 13.09 7.00 0.010 W: 0.82 Tr: 0.58 31 0.010 2.56 0.24 0.028 0.006 14.56 6.37 0.009 Co: 2.31 Al: 0.70 31 0.040 1.39 0.27 0.037 0.009 12.82 6.12 0.014 Cu: 0.91, W: 1.97 Tr: 0.81 32 0.026 4.12 0.30 0.023 0.009 13.12 7.12 0.014 Cu: 0.91, W: 1.97 Tr: 0.81 A 0.035 0.21 0.004 11.79 4.42 0.009 Tr: 0.81 B 0.046 0.31 0.21 0.004 11.72 5.26 0.011 C<		56	0.038	1,52	0.21	0.027	0.011	13.87	7.02	0.008		ï		16.3
28 0.007 2.04 0.30 0.032 0.012 12.18 5.40 0.011 Cu: 2.03 Nb: 0.45 29 0.013 0.37 0.26 0.028 0.008 13.09 7.00 0.010 W: 0.82 Ti: 0.58 30 0.010 2.56 0.24 0.028 0.005 14.56 6.37 0.009 Co: 2.31 AI: 0.70 31 0.040 1.39 0.27 0.037 0.009 12.82 6.12 0.014 Cu: 0.91, W: 1.97 Ti: 0.81 32 0.026 4.12 0.30 0.023 0.008 13.12 7.12 0.014 Cu: 0.91, W: 1.97 Ti: 0.81 A 0.035 0.21 0.16 0.021 0.004 11.79 4.42 0.009 C 0.009 0.45 0.40 0.021 0.004 11.72 5.01 0.013 D 0.014 0.28 1.32 0.019 0.007 10.86 3.97 0.025 E 0.013 0.57 1.49 0.028 0.007 17.53 7.40 0.094 F 0.058 0.51 1.14 0.025 0.005 17.44 7.10 0.070		27	0.007	3.05	0.31	0.024	0.008	13.16	6.33	0.015	Mo: 1.17		_	15.3
29 0.013 0.37 0.26 0.028 0.008 13.09 7.00 0.010 W: 0.82 Ti: 0.58 30 0.010 2.56 0.24 0.028 0.005 14.56 6.37 0.009 Co: 2.31 AI: 0.70 31 0.040 1.39 0.27 0.037 0.009 12.82 6.12 0.014 Cu: 0.91, W: 1.97 Ti: 0.81 32 0.026 4.12 0.30 0.023 0.009 13.12 7.12 0.014 Cu: 0.91, W: 1.97 Ti: 0.81 A 0.035 0.21 0.16 0.009 13.12 7.12 0.014 Cu: 0.91, W: 1.97 Ti: 0.81 B 0.046 0.31 0.21 0.004 11.72 4.42 0.009 Ti: 0.27 C 0.009 0.45 0.40 0.021 0.004 11.72 5.26 0.011 Nb: 0.40 D 0.014 0.28 1.32 0.019 0.007 10.86 3.97 0.025 F 0.058 </td <td></td> <td>78</td> <td>0.00</td> <td>2.04</td> <td>0.30</td> <td>0.032</td> <td>0.012</td> <td>12.18</td> <td>5.40</td> <td>0.011</td> <td>Cu: 2.03</td> <td></td> <td>ភ</td> <td>4.4</td>		78	0.00	2.04	0.30	0.032	0.012	12.18	5.40	0.011	Cu: 2.03		ភ	4.4
30 0.010 2.56 0.24 0.028 0.005 14.56 6.37 0.009 Co: 2.31 AI: 0.70 31 0.040 1.39 0.27 0.037 0.009 12.82 6.12 0.014 Cu: 0.91, W: 1.97 TI: 0.81 32 0.026 4.12 0.30 0.023 0.008 13.12 7.12 0.014 A 0.035 0.21 0.16 0.021 0.004 11.79 4.42 0.009 C 0.009 0.45 0.40 0.021 0.004 11.75 5.26 0.011 D 0.014 0.28 1.32 0.019 0.007 10.86 3.97 0.025 E 0.013 0.57 1.49 0.028 0.007 17.53 7.40 0.094 F 0.058 0.51 1.14 0.025 0.005 17.44 7.10 0.070		53	0.013	0.37	0.26	0.028	0.008	13.09	7.00	0.010	W: 0.82		38	14.7
31 0.040 1.39 0.27 0.037 0.009 12.82 6.12 0.014 Cu. 0.91, W: 1.97 Ti: 0.81 32 0.026 4.12 0.30 0.023 0.008 13.12 7.12 0.014 Cu. 0.91, W: 1.97 Ti: 0.81 A 0.026 4.12 0.008 13.12 7.12 0.014 Cu. 0.91, W: 1.97 Ti: 0.27 B 0.046 0.31 0.16 0.021 0.004 11.72 5.01 0.013 Nb: 0.40 C 0.009 0.45 0.40 0.021 0.004 11.72 5.26 0.011 Nb: 0.40 D 0.014 0.28 0.40 0.021 0.004 11.72 5.26 0.011 Nb: 0.40 E 0.013 0.57 1.49 0.026 17.75 7.40 0.094 17.53 7.40 0.094 F 0.058 0.51 1.14 0.025 0.005 17.44 7.10 0.070		30	0.010	2.56	0.24	0.028	0.005	14.56	6.37	0.009	Co: 2.31		2	15.1
32 0.026 4.12 0.30 0.023 0.008 13.12 7.12 0.014 A 0.035 0.21 0.16 0.021 0.004 11.79 4.42 0.009 Tr. 0.27 B 0.046 0.31 0.21 0.018 0.006 11.52 5.01 0.013 Nb. 0.40 C 0.009 0.45 0.40 0.021 0.004 11.72 5.26 0.011 Nb. 0.40 D 0.014 0.28 1.32 0.019 0.007 10.86 3.97 0.025 E 0.013 0.57 1.49 0.028 0.007 17.53 7.40 0.094 F 0.058 0.51 1.14 0.025 0.005 17.44 7.10 0.070		8	0.040	1.39	0.27	0.037	0.00	12.82	6.12	0.014	0.91, W:	Ë	31.	16.1
A 0.035 0.21 0.16 0.021 0.004 11.79 442 0.009 Ti: 0.27 B 0.046 0.31 0.21 0.018 0.006 11.52 5.01 0.013 Nb: 0.40 C 0.009 0.45 0.40 0.021 0.004 11.72 5.26 0.011 D 0.014 0.28 1.32 0.019 0.007 10.86 3.97 0.025 E 0.013 0.57 1.49 0.028 0.007 17.53 7.40 0.094 F 0.058 0.51 1.14 0.025 0.005 17.44 7.10 0.070		35	0.026	4.12	0.30	0.023	0.008	13.12	7.12	0.014				16.0
B 0.046 0.31 0.21 0.018 0.006 11.52 5.01 0.013 Nb: 0.40 C 0.009 0.45 0.40 0.021 0.004 11.72 5.26 0.011 D 0.014 0.28 1.32 0.019 0.007 10.86 3.97 0.025 E 0.013 0.57 1.49 0.028 0.007 17.53 7.40 0.094 F 0.058 0.51 1.14 0.025 0.005 17.44 7.10 0.070	ative	∢	0.035	0.21	0.16	0.021	0.004	11.79	4.42	0.00			7.2	10.5
0.009 0.45 0.40 0.021 0.004 11.72 5.26 0.011 0.014 0.28 1.32 0.019 0.007 10.86 3.97 0.025 0.013 0.57 1.49 0.028 0.007 17.53 7.40 0.094 0.058 0.51 1.14 0.025 0.005 17.44 7.10 0.070		8	0.046	0.31	0.21	0.018	9000	11.52	5.01	0.013			0:	Ξ
0.014 0.28 1.32 0.019 0.007 10.86 3.97 0.025 0.013 0.57 1.49 0.028 0.007 17.53 7.40 0.094 0.058 0.51 1.14 0.025 0.005 17.44 7.10 0.070		ပ	0.009	0.45	0.40	0.021	0.004	11.72	5.26	0.011				12.1
0.013 0.57 1.49 0.028 0.007 17.53 7.40 0.094 0.058 0.51 1.14 0.025 0.005 17.44 7.10 0.070		0	0.014	0.28	1.32	0.019	0.007	10.86	3.97	0.025				Ξ
0.058 0.51 1.14 0.025 0.005 17.44 7.10 0.070		ш	0.013	0.57	1.49	0.028	0.007	17.53	7.40	0.094			•	20.0
		u.	0.058	0.51	1.14	0.025	0.005	17.44	7.10	0.070				19.7

TABLE 2

Mechanical properties and amount of martensite of products of the invention process and comparative products

		mar. (%)	96 888 887 77 77 80 80 80 80 80 80 80 80 80 80 80 80 80	9666 8666
	(()	¥	337 339 331 331 331 331 332 332 332 333 333 331 332 332	297 300 294 307
	10 hr. ((a	E! (%)	78.60.00 78.60.	6.8 7.0 5.9
	600°C × 10 hr. ((a))	σ _B (kg/mm²)	100 100 100 100 100 100 100 100 100 100	96 96 98 88
Invention Process		^{σ_{0.2} (kg/mm²)}	001 002 007 007 007 007 007 007 007 007 007	83 83 85 85
nventio	_	mar. (%)	99 99 99 99 99 99 99 99 99 99 99 99 99	00000
`	aled (d)	Ž.	332 2318 2318 2318 232 233 233 233 233 233 335 336 337 337 337 337 337 337 337 337 337	302 304 296 297
	As Anne	E! (%)	6.5.5.4 6.5.4 6.	7.3
	$C \times 10$ hr. (As Annealed (d))	σ _B (kg/mm²)	011 010 010 010 010 010 010 010 010 010	97 95 95 95
	2.009	^{σ_{0.2} (kg/mm²)}	82574767777777778888847746878888 60 60 60 60 60 60 60 60 60 60 60 60 60	8888
		mar. (%)	000000000000000000000000000000000000000	100 100 100 21 18
ess	_	¥	332 332 333 333 333 333 333 333 333 333	330 326 307 342 342
nal Proc	ealed (d,	E/ (%)	$\frac{44}{6}$	6.0 5.7 5.9 26.3
Conventional Process	As Annealed (d,	σ _в (kg/mm²)	221 221 201 201 201 201 201 201 201 201	105 103 97 105 96 109
		_{σο2} (kg/mm²)	21 121 121 122 123 124 125 125 125 125 125 125 125 125 125 125	94 96 89 72 70
	Sample No.	•	- 264597860112545578605586055860558605586055860558605586	4 m O O m ir
20			Products of the Invention Process	Compara- tive Products

TABLE 2—continued

Invention Process

_	mar. (%)	995 4 4 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8	6 566
)% Cold)	Hv	3330 3300 3300 3300 3300 3300 3300 330	315 302 320 320
((c)) (2((%)	44. 44. 46. 46. 46. 46. 46. 46.	0.88.0 0.40.00
600°C × 10 hr. ((c)) (50% Cold)	σ _B (kg/mm²)	110 99 99 99 99 99 99 99 99 99 99 99 99 99	103 97 98 104
009	^{σ_{0.2} (kg/mm²)}	0.00	888 895 895
_	mar. (%)	1083822002208862508886250888428884288868888888888888888888888888	9999
3% Cold,	H	289 289 301 301 289 290 291 291 291 291 291 291 306 306 306 306 306 306 307 306 307 307 307 307 307 307 307 307 307 307	298 305 300 318
((9))	(%)	16.2 19.2 19.2 19.2 19.2 19.2 19.3 19.3 19.3 19.3 19.3 19.3 19.3 19.3	8.3 7.3 7.3
600°C × 10 hr. ((b)) (83% Cold)	σ _в (kg/mm²)	10101 0101 0101 0101 0101 0101 0101 01	99 94 90 90
009	^{σ_{0.2} (kg/mm²)}	100 888 888 888 888 888 888 888 888 888	85 83 87
Sample	No.	-28489786012845978688868888888888888888888888888888888	A അ റ O m ir
•		Steels for the Invention Process	Compara- tive Steels

TABLE 3

Mechanical properties and amount of martensite of the products of the invention process and the products of the comparative process (annealed materials)

		mar. (%)	82	82	75	72	73	75	80	84	71	83	72	95
		H	276	291	293	284	285	281	283	300	328	321	303	353
٠	600°C × 20 hr.	E1 (%)	17.3	18.4	18.5	18.0	18.9	18.7	19.3	19.1	17.4	18.5	19.4	17.3
	2.009	σ _B (kg/mm²)	84	88	90	87	90	93	88	92	117	108	96	113
·		_{60.2} (kg/mm²)	71	75	89	75	20	72	73	82	86	82	78	100
		mar. (%)	96	97	6	6	6	96	96	93	6	95	97	92
જ		H _v	290	311	300	322	283	298	340	337	330	325	316	358
Invention Process	575°C × 5 hr.	EI (%)	15.3	15.4	14.9	15.5	14.9	15.3	15.1	15.0	15.6	14.8	15.4	15.3
Inventio	275.0	σ ₈ (kg/mm²)	86	106	<u> </u>	<u> </u>		8 8	3 5	110	110	106	5 5	117
		$\sigma_{0.2}$ (kg/mm²)	11.	. 6	3 8	8 &	3 %	2 6	£	10.5	68	9 5	6	88
		mar. (%)	8	8 8	8 8	6	5 6	à ö	8 8	8 6	8 8	8 8	8 8	8 6
		Ħ	286	200	- 62	213	5 6	201	322	320	334	326 326	200	356
	550°C × 30 hr.	E! (%)			- u	10.4	t 0	0 0	16.0	- 6	2 4	- T		13.3
	550°C	σ _B (kg/mm²)	0	3 8	۵ ۵	S 6	60	4 C	0 d	<u> </u>	3 :		2 8	119
		$\sigma_{0.2}$ (kg/mm^2) (,	† 6	S 1	e 6	0 r	e 6	Q 6	6 6	5 6	† u	2 8	97
	Sample	No.	c	· ·	4 (ه م	ກຸ	7.	 	<u>+</u> 6	ם צ	C7 5	97	32

TABLE 3—continued

ducts of the invention process and the products of the comparative process (annealed materials)

				-	Inventio	Invention Process						Comparative Process	ive Proce	SS	
Sample		625°C	625°C × 1 hr.				2.529	675°C × 1 hr.				710°C	710°C × 1 hr.		
No.	σ _{α2} (kg/mm²)	σ _{o2} σ _B Kg/mm²) (kg/mm²)	E! (%)	H	mar. (%)	$\sigma_{0.2}$ (kg/mm²)	σ _в (kg/mm²)	E/ (%)	Ã	mar. (%)	σ _{0.2} (kg/mm²)	σ _B (kg/mm²)	E! (%)	Ŧ,	mar. (%)
	į	ć	,	2	6	. 2	5	149	298	83	52	88	11.0	281	78
က	29	93	7.01	\$ 5	8 6	† u	5,6) c	202	6	54	86	10.7	287	79
4	29	97	16.7	319	9 ;	င္ (၀)	n 0	5 6	200	7 6	5 6	, K	116	261	99
9	92	. 87	17.1	282	20	63	£8	9.9	767	2 1	3 6	3 6			8
σ	74	88	16.9	290	69	7	88	16.4	289	9	ရှင် ရ	λ č	5.5	7/7	† c
. 5	8	85	18.0	288	89	64	9	17.5	290	2	20	<u>ه</u>	17.1	007	70 6
<u> </u>	5 62) 	18.9	283	71	73	92	16.3	281	17	26	87	11.3	526	? ;
- ÷	7 7	, K	196	279	73	11	93	16.9	283	69	09	82	12.5	278	ς ;
<u> </u>	, 6	90	19.8	308	8	89	94	16.4	295	75	61	91	10.8	290	9.
ָם - כ	n (, t	, a	310	67	62	109	15.9	309	72	61	110	11.7	286	92
c 7	3 8	+ C	- u	2 5	8	2 6	103	15.7	308	71	28	66	10.8	276	83
87 7	70	8 8	2 0	5 6	9 4	75	8	17.0	289	69	22	82	12.6	271	62
5	4/	20	C'07	£07	3 3	2 1	, t		20.	4	æ	117	9.2	310	2
32	101	116	20.2	363	5	6/	<u>Ω</u> -	- - - -	351	2	3	• •	!		



CLAIMS

5	1. Process for preparing a high strength stainless steel material having excellent workability free from weld softening consisting of a single martensitic phase or a duplex phase structure of martensite and minute austenite, said process comprising heat-treating at a temperature of 550 to 675°C for 1 to 30 hours a hot-rolled, cold-rolled	5
	or annealed material of a steel essentially consisting of:	
	C: not more than 0.10%	
•	Si: 0.20 – 4.5%	
	Mn: 0.20 – 5.0%	
10	P: not more than 0.060%	10
10	S: not more than 0.030%	
•	Cr: 10.0 – 17.0%	
	Ni: 3.0 – 8.0%	
	N: 0.0 = 0.0 % N: not more than 0.10%	
1 5	and Fe and inevitable incidental impurities, wherein the Ni_{eq} Value defined as: $Ni_{eq} = Ni + Mn + 0.5Cr +$	15
15	0.3Si + 20(C + N) is in the range of $13.0 - 17.5$.	
	2. The process for preparing a high strength steel material as set forth in Claim 1, wherein the steel essentially	
	consists of: C: 0.005 – 0.08%	
		20
20	Si: 0.25 – 4.0%	20
	Mn: 0.30 – 4.5%	
	P: not more than 0.04%	
	S: not more than 0.02%	
	Cr: 11.0 - 16.0%	05
25		25
	N: not more than 0.07%	
	and Fe and inevitable incidental impurities.	
	3. The process for preparing a high strength steel material as set forth in Claim 2, wherein the steel essentially	
	consists of:	
30	•	30
	Si: 0.40 – 4.0%	
	Mn: 0.40 – 4.0%	
	P: not more than 0.035%	
	S: not more than 0.015%	
35		35
	Ni: 4.0 – 7.5%	
	N: not more than 0.05%	
	and Fe and inevitable incidental impurities.	
	4. Process for preparing a high strength stainless steel material having excellent workability and free from	
40	weld softening consisting of a single martensitic phase or a duplex phase structure of martensite and minute	40
	austenite, said process comprising heat-treating at a temperature of 550 to 675°C for 1 to 30 hours a hot-rolled,	
	cold-rolled or annealed material of a steel essentially consisting of:	
	C: not more than 0.10%	
	Si: 0.2 – 4.5%	
45	, , , , , , , , , , , , , , , , , , , ,	45
	P: not more than 0.060%	
	S: not more than 0.030%	
	Cr: 10.0 – 17.0%	
	Ni: 3.0 – 8.0%	
50	N: not more than 0.10%	50
	At least one of Cu, Mo, W and Co: not more than 4% in total and Fe and inevitable incidental impurities,	
	wherein the Ni _{eq} value defined as:	
	$Ni_{eq} = Ni + Mn + 0.5Cr + 0.3Si + 20(C + N)$	
	+ Cu + Mo + W + 0.2Co	
55	is is in the range of 13.0 – 17.5.	55
	5. The process for preparing a high strength stainless steel material as set forth in Claim 4, wherein the steel	
	essentially c nsists of:	
	C: 0.005 – 0.08%	
	Si: 0.25 – 4.0%	
60		60
	P: not more than 0.04%	-
	S: not mor than 0.020%	
	Cr: 11.0 – 16.0%	
	Ni: 3.5 – 7.5%	
69		65
- •		

At least one of Cu, Mo, W and Co: 0.5 - 3.5% in total and Fe and inevitable incidental impurities. 6. The process for preparing a high strength stainless steel material as set forth in Claim 5, wherein the steel essentially consists of: C: 0.007 - 0.06% 5 Si: 0.40 - 4.0% Mn: 0.40 - 4.0% P: not more than 0.035% S: not more than 0.015% 10 Cr: 12.0 - 15.0% 610 Ni: 4.0 - 7.5% N: not more than 0.05% At least one of Cu, Mo, W and Co: 1.0 - 3.0% in total and Fe and inevitable incidental impurities. 15 7. Process for preparing a high strength stainless steel material having excellent workability and free from weld softening consisting of a single martensitic phase or a duplex phase structure of martensite and minute austenite, said process comprising heat-treating at a temperature of 550 to 675°C for 1 to 30 hours a hot-rolled, cold-rolled or annealed material of a steel essentially consisting of: C: not more than 0.10% 20 20 Si: 0.2 - 4.5% Mn: 0.2 - 5.0% P: not more than 0.060% S: not more than 0.030% Cr: 10.0 - 17.0% 25 25 Ni: 3.0 - 8.0% N: not more than 0.10% At least one of Ti, Nb, V, Zr, Al and B: not more than 1% in total and Fe and inevitable incidental impurities, wherein the Nieq value defined as: $Ni_{eq} = Ni + Mn + 0.5Cr + 0.3Si$ is in the range of 13.0 – 17.5. 30 8. The process for preparing a high strength stainless steel material as set forth in Claim 7, wherein the steel essentially consists of: C: 0.005 - 0.08% Si: 0.25 - 4.0% Mn: 0.30 - 4.5% 35 P: not more than 0.04% S: not more than 0.02% Cr: 11.0 - 16.0% Ni: 3.5 - 7.5% N: not more than 0.07% At least one of Ti, Nb, V, Zr, Al and B: 0.1 – 0.8% in total and Fe and inevitable incidental impurities. 40 9. The process for preparing a high strength stainless steel material as set forth in Claim 8, wherein the steel essentially consists of: C: 0.007 - 0.06% Si: 0.40 - 4.0% 45 45 Mn: 0.40 - 4.0% P: not more than 0.035% S: not more than 0.015% Cr: 12.0 - 15.0% Ni: 4.0 - 7.5% 50 N: not more than 0.05% At least one of Ti, Nb, V, Zr, Al and B: 0.15 - 0.8% in total and Fe and inevitable incidental impurities. 10. Process for preparing a high strength stainless steel material having excellent workability and free from weld softening consisting of a single martensitic phase or a duplex phase structure of martensite and minute austenite, said process comprising heat-treating at a temperature of 550 to 675°C for 1 to 30 hours a hot-rolled, 55 55 cold-rolled or annealed material of a steel essentially consists of: C: not more than 0.10% Si: 0.20 - 4.5% Mn: 0.20 - 5.0% P: not more than 0.060% 60 60 S: not more than 0.030% Cr: 10.0 - 17.0% Ni: 3.0 - 8.0% N: not more than 0.10% At least one of Cu, Mo, W and Co: not more than 4% in total 65 At least one of Ti, Nb, V, Zr, Al and B; not more than 1% in total and Fe and inevitable incidental impurities, 65



٧	wherein the Ni _{ea} value defined as:	
	$Ni_{en} = Ni + Mn + 0.5Cr + 0.3Si + Cu + Mo + W + 0.2Co$ is in the range of 13.0 – 17.5.	
	11. The process for preparing a high strength stainless steel material as set forth in Claim 10, wherein the	
S	steel essentially consists of:	
5	C: 0.005 – 0.08%	· 5
	Si: 0.25 – 4.0%	
	Mn: 0.30 – 4.5%	
	P: not more than 0.040%	
	S: not more than 0.020%	
10	Cr: 11.0 – 16.0%	10
	Ni: 3.5 – 7.5%	
	N: not more than 0.07%	
	At least one of Cu, Mo, W and Co: 0.5 – 3.5% in total	
	At least one of Ti, Nb, V, Zr, Al and B: 0.1 – 0.8% in total and Fe and inevitable incidental impurities.	
15	12. The process for preparing a high strength stainless steel material as set forth in Claim 11, wherein the	15
	steel essentially consists of:	
	C: 0.007 - 0.06%	
	Si: 0.40 – 4.0%	
	Mn: 0.40 – 4.0%	
20	P: not more than 0.035%	20
	S: not more than 0.015%	
	Cr: 12.0 – 15.0%	
	Ni: 4.0 – 7.5%	
	N: not more than 0.05%	
25	At least one of Cu, Mo, W and Co: 1.0 – 3.0% in total	25
	At least one of Ti. Nb. V. Zr. Al and B: 0.15 – 0.8% in total and Fe and inevitable incidental impurities	

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